RESEARCH PAPER | Education | Volume : 4 | Issue : 10 | October 2014 | ISSN - 2249-555X

Association Thermodynamic Parameters (Conductmetrically) for Nano Copper Sulfate in Mixed DMF–H_2o Solvents at Different Temperatures

KEYWORDS: Thermodynamics, molar conductance, nano copper sulfate, free energy, enthalpy, entropy of association, mixed DMF – H_2O solvents.

Mohamed N .H. Hamed

Faculty of Education, Chemistry Department, Ain Shams University, Roxy, Cairo, Egypt

ABSTRACT *The molar conductance for Nano copper sulfate (CuSO4) in different percentages of dimethylformamide (DMF) and water were measured at 292.15, 303.15, 308.15 and 313.15K. From the molar conductance for Nano $CuSO_4$, the solvation parameters like, activity coefficient, association constant, free energy of assocation, enthalpy of association and entropy of association were estimated. All these solvation parameters were discussed.*

1. Introduction:

Copper sulfate pentahydrate is a fungicide. However, some fungi are capable of adapting to elevated levels of copper ions. Mixed with lime it is called Bordeaux mixture and used to control fungus on grapes, melons, and other berries. Copper ions are highly toxic to fish, so care must be taken with the dosage. Most species of algae can be controlled with very low concentrations of copper sulfate. Copper sulfate inhibits growth of bacteria [1] and can cause cell death.Heavy metals causes cancer and changes in hormone balance and hyperthermia. copper salts can form the two types of cell death [2].

Our purpose is to try to estimate different concentrations of Nano copper sulfate to get rid from body and environment.

2. Experimental

2.1. Materials

$CuSO_4$ from Al Nasr chemicals Co. was used without purification.

DMF of the type Adwic was used.

2.2. Preparation of Nano $CuSO_4$

$CuSO_4$ of the type Adwic was milled by ball - mill. The ball – mill was a Retsch MM2000 swing mill with 10 cm^3 stainless steel , double – walled tube. Two stainless steel balls of 12mm diameter and 7 gm weight for each were used. Ball-milling was performed at 20225 Hz for half an hour at room temperature (without circulating liquid and the temperature did not rise above 30°C).

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction of Nano copper sulfate in Fig. (1) shows that it has about 100% of the structure is $CuSO_4$. The axial ratio of a : b : c is 0.519 : 1.000 : 0.5579 . The crystal system is triclinic – pinacoidal, the cell dimensions are : a = 6.12 , b = 10.7 , c = 5.97, z = 2 , v = 361.55, alpha =97.583 , beta = 107.167 and gamma = 77.55 . The forms are (0 2 1) (0 1 0) (1 3 0) (1 1 0) (1 1 1) (1 0 0) . The density calculated = 2.29 . The cleavage is { 1 1 0 } imperfect , { 1 1 0 } indistinct and { 1 1 1 } indistinct .

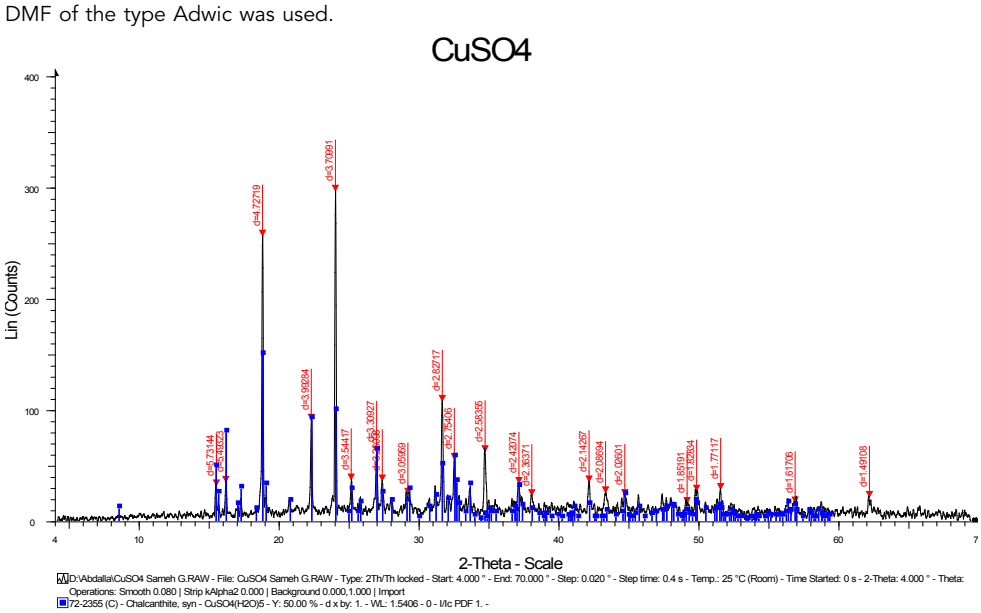


Figure (1) X-ray diffraction of Nano copper sulfate

Volume : 4 | Issue : 10 | October 2014 | ISSN - 2249-555X

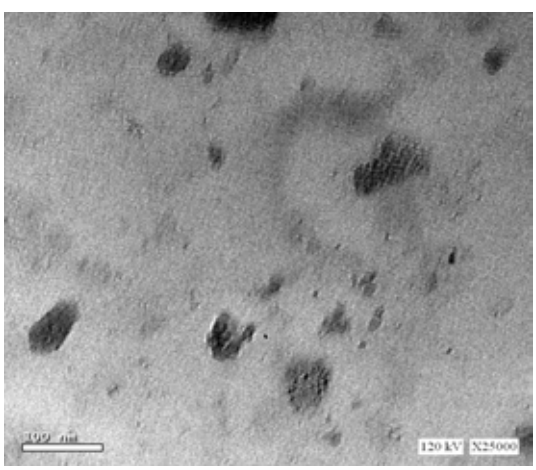
Conductometric measurments

In 5 ml of the $CuSO_4$ solution (1.0 x 10^{-3} M) was placed in the titration cell, thermostated at the preset temperature and the conductance of the solution was measured after the solution reached thermal equilibrium. Then, a known amount of solvent was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition until the desired constant reading was achieved. The specific conductance values were recorded using conductivity bridge JENCO – 3173 COND. with a cell constant equal to 1. The conductometer was conducted with a thermostat of the type the Kottermann 4130 ultra thermostat. The temperature was adjusted at 293.15, 298.15, 303.15 and 308.15 K.

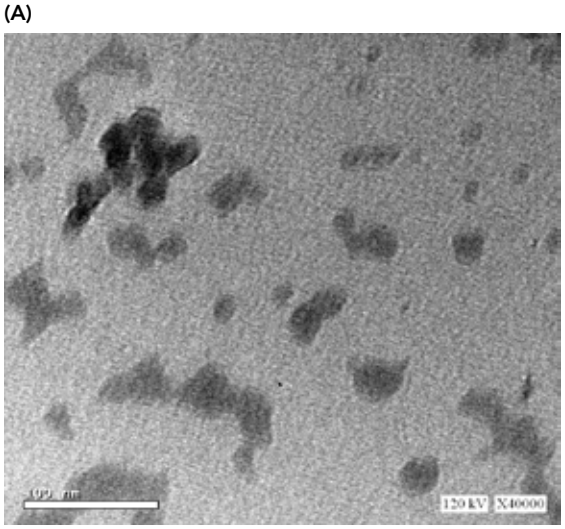
Results and discussion

TEM Imagies

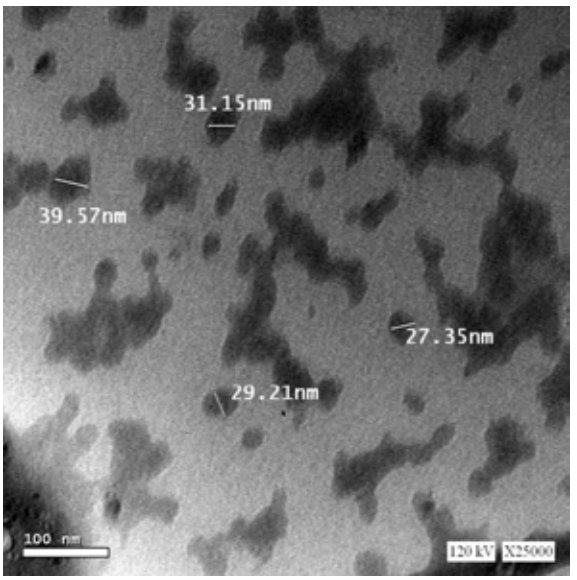
Fig. (**2**) in all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of $CuSO_4$ obtained in ethanol are irregular spheres in the form of cylinders. The diameter in the range of 10-77.86 nm.The small sizes in the range between 10, 12.05 to 20.76 nm are collected to give bigger sizes till 77.86 nm. These different sizes were proved also by x- ray diffraction which gave crystal sizes in the same order .The non homogeneity in sizes for Nano copper sulfate need controlling during the primary preparation of the samples.



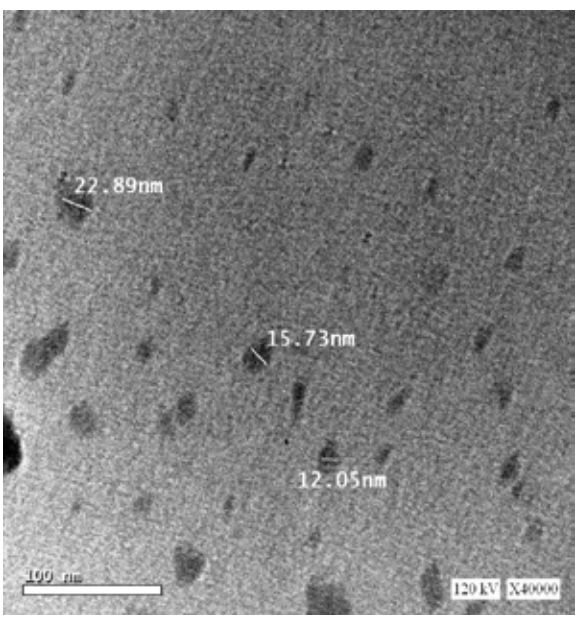
(A)



(B)



(C)



(D)

Fig.2 : TEM for Nano copper sulfate

Association parameters:

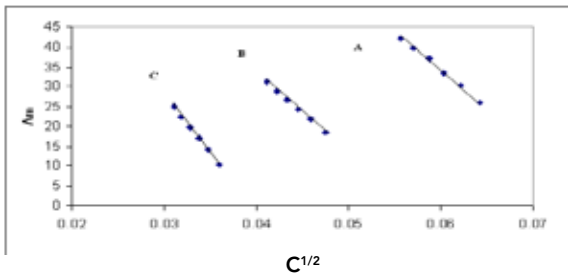
The molar conductance (Λ_m) values were calculated using equation (1) [1-20]:

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \qquad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively ; K_{cell} is the cell constant and C is the molar concentration of the $CuSO_4$ solution.

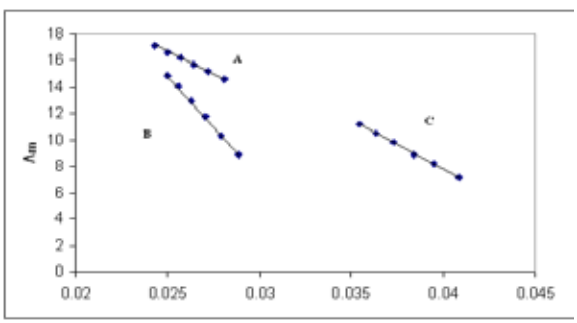
By drawing the relation between molar conductance ($/\backslash_m$) and $C^{1/2}$,straight lines were obtained from which we extrapolate the line to zero salt concentration to evaluate the limiting equivalent conductansce. Figures (3) and (4) show the relation between ($/\backslash_m$) and $C^{1/2}$.

Volume : 4 | Issue : 10 | October 2014 | ISSN - 2249-555X



$C^{1/2}$

Line (A) : 50% DMF – 50% H_2O
Line (B) : 60% DMF – 40% H_2O
Line (C): 70% DMF – 30% H_2O
Fig. (3) The relation between ($/\__m$) and $C^{1/2}$.



$C^{1/2}$

Line (A): 80% DMF – 20% H_2O
Line (B): 90% DMF – 10% H_2O
Line (C): 100% DMF –0% H_2O
Fig. (4) The relation between (Λ_m) and $C^{1/2}$.

The association constant K_A was calculated by using equation (2) and the evalualted values are listed in Figures (5) and (6) and Tables 1,2,3 and 4 at the different temperatures 292.15 , 303.15 . 308.15 and 313.15K.

$$K_A = \frac{\Lambda_0 (\Lambda_0 - S(Z)\,\Lambda_m)}{C_m \Lambda_m^2 S(Z)^2\, \gamma_\pm^2} \qquad (2)$$

Table (1) : Association constants K_A and Gibbs free energies of association (ΔG_A) for Nano $CuSO_4$ in mixed DMF –H_2O solvent at 292.15K.

X_s	C_m	Λ_m	Λ_0	log $\gamma_\pm$	K_A	ΔG_A
0.1894	6.6133 x 10^{-4}	98	148	-0.0130	1237.0016	-17.2686
0.2595	6.6133 x 10^{-4}	64	117	-0.0130	2430.4824	-18.9066
0.3528	6.6133 x 10^{-4}	42	95	-0.0130	4582.3851	-20.4445
0.4831	6.6133 x 10^{-4}	16.17	33	-0.0130	3677.1722	-19.9112
0.6774	6.6133 x 10^{-4}	13.8	61	-0.0130	24271.932	-24.4882
1.0000	6.6133 x 10^{-4}	20	42.4	-0.0130	3811.9270	-19.9983

Table (2) : Association constants K_A and Gibbs free energies of association (ΔG_A) for Nano $CuSO_4$ in mixed DMF –H_2O solvent at 303.15K.

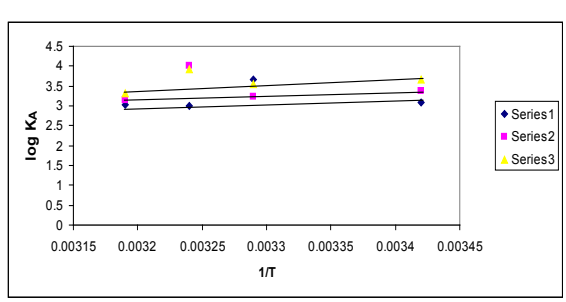
X_s	C_m	Λ_m	Λ_0	log $\gamma_\pm$	K_A	ΔG_A
0.1894	1.0573 x 10^{-3}	55.33	149	-0.0164	4650.5556	-21.2776
0.2595	1.0573 x 10^{-3}	66	125	-0.0164	1727.0843	-18.7817
0.3528	1.0573 x 10^{-3}	32.5	79	-0.0164	3547.7476	-20.5953
0.4831	1.0573 x 10^{-3}	20	51	-0.0164	4031.9141	-20.9178
0.6774	1.0573 x 10^{-3}	17.4	37.4	-0.0164	2520.2434	-19.7337
1.0000	1.0573 x 10^{-3}	16	35.5	-0.0164	2758.4329	-19.9612

Table (3) : Association constants K_A and Gibbs free energies of association (ΔG_A) for Nano $CuSO_4$ in mixed DMF –H_2O solvent at 308.15K.

X_s	C_m	Λ_m	Λ_0	log $\gamma_\pm$	K_A	ΔG_A
0.1894	1.9971 x 10^{-3}	36	71	-0.0226	1011.3887	-17.7209
0.2595	1.9971 x 10^{-3}	18.07	87.5	-0.0226	10337.895	-23.6743
0.3528	1.9971 x 10^{-3}	15	65.5	-0.0226	8168.5201	-23.0710
0.4831	1.9971 x 10^{-3}	27	55	-0.0226	1173.7792	-18.1019
0.6774	1.9971 x 10^{-3}	13.8	35.5	-0.0226	2247.6213	-19.7661
1.0000	1.9971 x 10^{-3}	13.8	40	-0.0226	3057.7103	-20.5440

Table (4) : Association constants K_A and Gibbs free energies of association (ΔG_A) for Nano $CuSO_4$ in mixed DMF –H_2O solvent at 313.15K.

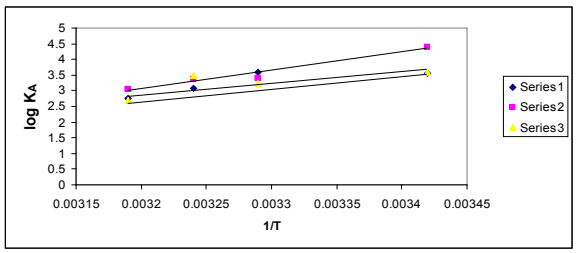
X_s	C_m	Λ_m	Λ_0	log $\gamma_\pm$	K_A	ΔG_A
0.1894	1.8796 x 10^{-3}	51.20	100	-0.0219	1095.5598	-18.2164
0.2595	1.8796 x 10^{-3}	43.2	92	-0.0219	1415.7820	-18.8834
0.3528	1.8796 x 10^{-3}	27.8	67.5	-0.0219	2040.6142	-19.8351
0.4831	1.8796 x 10^{-3}	17.62	28	-0.0219	550.9342	-16.4269
0.6774	1.8796 x 10^{-3}	11.95	23.3	-0.0219	1089.6370	-18.2020
1.0000	1.8796 x 10^{-3}	14.2	22	-0.0219	500.8374	-16.1788



Series 1 : 50% DMF – 50% H_2O

Volume : 4 | Issue : 10 | October 2014 | ISSN - 2249-555X

Series 2 : 60% DMF – 40% H_2O
Series 3 : 70% DMF – 30% H_2O
Fig. (5) : The relation between K_A and 1/T



Series 1 : 80% DMF – 20% H_2O
Series 2 : 90% DMF – 10% H_2O
Series 3 : 100% DMF –0% H_2O
Fig. (6) : The relation between K_A and 1/T

The Gibbs free energies of association for each were calculated by [20-30]:

$$\Delta G_A = - RT \ln K_A \qquad (3)$$

The calculated ΔG_A values are presented in Tables 1,2,3 and 4.

The enthalpy changes of association (ΔH_A) were calculated from the plots of log K_A against 1/T, (slope = -ΔH/2.303 R) (Fig. 5 and 6) using Van't Hoff eqn . [30-43] :

$$\log K_A = \frac{-\Delta H}{2.303R} \cdot \frac{1}{T} + \text{constant} \qquad (4)$$

Where R is the gas constant and T is the absolute temperature.

Entropy ΔS were for association calculated [8] by using Gibbs-Helmholtz equation (7) [35-41] :

$$\Delta G_A = \Delta H_A - T\Delta S_A \qquad (5)$$

The calculated values of (ΔH_A) and (ΔS_A) for $CuSO_4$ were tabulated in Table (5):

Enthalpies and entropies of association data are calculated as given before and their data are tabulated in Table (5) at 313.15K.

Table (5) : Enthalpies and entropies of association for Nano copper sulfate at 313.15K.

X_s	ΔH_s (kJ/mole)	TΔS
0.1894	-21.8319	-3.68155
0.2595	-9.2925	9.5909
0.3528	-16.3555	3.4796
0.4831	-68.6053	-52.1784
0.6774	-112.1565	-93.9545
1.0000	-73.3481	-57.1693

Conclusion

This research focused on the study of conductance measurements for Nano $CuSO_4$. The stability constants of association were measured by applying the conductometric method at different temperatures. Based on the results, the association constrant increase with increase of DMF and decrease with increasing temperatures indicating increase in association on adding DMF in solution and deacrese by raising temperatute due to the increase in the kinetic energy.

REFERENCE

[1] David A. Wright and Pamela Welbourn , Cambridge Environmental Chemistry Series 111 , Cambridge University press , Cambridge UK (2002) . | [2] F.I.El - Dossouki, Chemistry Department, Faculty of Science , Mansoura University,Ph.D.thesis, 1999 | [3] M.V. Angelusiu, S.F. Barbuceanu, C. Draghici, G.L. Almajan, Eur. J. Med. Chem. 2010) 2055–2062. | [4] J.C. Skou, M. Esmann. Biochim. Biophys. Acta (BBA)-Biomembr., 1 (1981), pp. 101–107. | [5] J.C. Skou, M. Esmann. Biochim. Biophys. Acta (BBA), 727 (1) (1983), pp. 101–107. | [6] K.M., Tawarah, S.A.Mizyed : A conductance study of the association of alkali cations with 1,13-dibenzo-24-crown-8 in acetonitrile. J. Solution Chem. 18, 387–401 (1989). | [7] A.J.,Smetana, A.I., Popov, J. Chem. Thermodyn. 11, 1145–1149 (1979). | [8] P., Debye, H.Hückel, Phys. Z. 24, 305 (1923). | [9] Y. Takeda, , Bull. Chem. Soc. Jpn. 56, 3600–3602 (1983). | [10] D.P. Zollinger, E., Bulten, A., Christenhuse, A., Bos, ., W.E.Van Der Linden,: in polar solvents. Anal. Chim. Acta. 198, 207–222 (1987). | [11] Y.Takeda, Bull. Chem. Soc. Jpn.,56, 3600 (1983). | [12] Dye, J.L., Nicely, V.A.: A general purpose curve fitting program for class and research use. J. Chem. Educ. 48, 443 (1971). | [13]D.J.G.Ives, (1971), Chemical Thermodynamics, University Chemistry, Macdonald Technical and Scientific, New York. | [14] Esam A.Gomaa and R.M.Galal , Basic Sciences of Medicine, 1(2), (2012), 1-5. | [15] Esam A.Gomaa, Physics and Chemistry of Liquids, 50(2012)279-283. | [16] Esam A.Gomaa, International Journal of Materials and Chemisty, 2(1), (2012)16-18. | [17] Esam A.Gomaa, American Journal of Environmental Engineering, 2(3) , (2012)54-57. | [18] Esam A.Gomaa . American Journal of Polymer Science, 2(3) , (2012),35-38. | [19] Esam A.Gomaa. Eur. Chem. Bull., 1(2013) 259-261. | [20] Esam A.Gomaa, Elsayed abou Elleef and E.A.Mahmoud , Eur . Chem. Bull, 2(2013),732-735. | [21] Esam A Gomaa and Elsayed M.Abou Elleef , American Chemical Science Journal , 3(2013) , 489-499. | [22] Esam A. Gomaa , Elsayed M.Abou Elleef,Science and Technology, 3(2013)118-122. | [23] Esam A Gomaa and M.G.Abdel Razek , International Research Journal of Pure and Applied Chemistry,3(2013)320-329 | [24] Esam A.Gomaa , International Journal of Theoretical and Mathematical Physcics,3(2013)151-154. | [25] Esam A.Gomaa and B.A.Al Jahadali, Education., 2(3),(2012)37-40. | [26] Esam A Gomaa , American Journal of Biochemistry, 2(3), 92012),25-28. | [27] Esam A. Gomaa , Food and Public Health, 2(3),2012, 65-68. | [28] Esam A.Gomaa , Global Advanced Research Journal of Chemistry and Material Science, 1(2012)35-38. | [29]J.I. Kim, A. Cecal, H.J. Born, and E.A. Gomaa, Z. Physik Chemic, Neue Folge 110, 209(1978). | [30] J.I.Kim and E.A.Gomaa, Bull.Soci.Chim.Belg.,90(1981)391. | [31]E.A.Gomaa,A.A.El-Khouly and M.A.Mousa , Indian Journal of Chemistry , 23((1984)1033. | [32] E.A.Gomaa,M.A.Mousa and A.A.El-Khouly,Thermochimica Acta,86 (1985)351. | [33]E.A.Gomaa,M.A.Mousa and A.A.El-Khouly,Thermochimica Acta ,89(1985)133. | | [34] A.A.El-Khouly ,E.A.Gomaa and S.E.Salem, Southern Brazilian Journal of Chemistry ,vol.20 (2012)43-50. | [35 E.A.Gomaa and B.A.M.Al –Jahdali,American Journal of Environmrntal Engineering,2(2012)6-12. | [36] S.L. Oswal, J.S. Desai, S.P. Ijardar, and D.M. Jain, J. Mol. Liquids 144, 108 (2009). | [37] D. Bobicz, W. Grzybkowski, and A. Lwandowski, J. Mol. Liquids 105, 93 (2003). | [38] Y. Marcus. The Properties of Solvents (Wiley, London, 1998). | [39] E.A.Gomaa,M.A.Hamada and R.Galal,Avances en Quimica,5(2),117-121(2010). | [40] Esam A .Gomaa,Analele Uni.din Bucuresti-Chimie,vol.19 no1 ,pag.45-48(2010). | [41] Nagah A.El-Shishtawi,Maany A. Hamada and Esam A.Gomaa, Physical Chemistry,1(1),(2011,14-16. | [42] E.A.Gomaa and B.A.M.Al Jahdali,American Journal of Condenesed Matter Physics, 2(1),(2012),16-21. | [43] Corradini, F. marcdhetti, A., Tgagli Azucchi, M. , Tassi L., and Tosi, G., J. Chem. Soc., Faraday. Trans. , 89, 1359, (1993). |